AD NUMBER
AD008228
CLASSIFICATION CHANGES
TO: **unclassified**
FROM: **confidential**
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Controlling DoD Organization: Office of Naval Research, Arlington, VA 22203.**
AUTHORITY
ONR ltr dtd 10 Apr 1961; ONR ltr dtd 26 Oct 1977

AD _____

CONFIDENTIAL

COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

TELEPHONE CRAWFORD 7071

February 2, 1952
Copy No. 15

Report No. 3
(Quarterly Summary)

SUBJECT: CNR Nitropolymer Research

CONTRACT: Nonr-397(00)

PERIOD COVERED: October 15, 1951 to January 31, 1952

SUBMITTED BY: John T. Minor

APPROVED BY: Jerome Martin
Jerome Martin
Director of Research

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

SECURITY INFORMATION

CONFIDENTIAL

COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

RECEIPT FOR CLASSIFIED DATA

To: Commanding General
Wright-Patterson Air Force Base
Dayton, Ohio
Attn: WCEGH-2

Date: Feb. 15, 1952

Quan.	Report No.	Copy No.	Title
1	3	15	Quarterly Summary October 15, 1951 - January 31, 1952 ONR Nitropolymer Research Contract Nonr-397(00)

I have personally received the material described above and accept full responsibility for its safe handling, storage, and transmittal elsewhere in accordance with applicable Government regulations.

Return to:

Dr. Jerome Martin
Director of Research
Commercial Solvents Corporation
Terre Haute, Indiana

Signed 29 Feb 52
Charles J. Lloyd

_____
(Name of individual, firm, or corporation)

By: _____
(Signature)

_____
(Title)

_____
(Name typed or printed of official)

Date Received: _____

COMMERCIAL SOLVENTS CORP. Report No. 3

TABLE OF CONTENTS

COMMERCIAL SOLVENTS CORP. Report No. 3

CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of Contract Nonr-397(00).

COMMERCIAL SOLVENTS CORP. Report No. 3

I. SUMMARY

A. This quarterly summary report is the first under Contract Nonr-397(00) and covers the period from October 15, 1951 to January 31, 1952. The object of this contract is as follows: Shall conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the application of processes not now employed in the preparations.

B. The more important results and conclusions of the work reported are presented below:

1. 2-Nitroethanol has been prepared in average yields of 66%, based on the formaldehyde used, by a reflux method. A column serves as both rectifying and reaction tube. Purification was best achieved by azeotropic distillation with phenyl ether.

2. 2-Nitropropanediol-1,3 (NPD) has been prepared in 46% yield from nitromethane and formaldehyde. This is a two-step reaction, the sodium salt first being formed in 85-90% yield. The NPD is obtained by acidification of the sodium salt with 15% sulfuric acid in the presence of urea and extracting with ethyl acetate.

3. By the base catalyzed condensation of nitromethane and formaldehyde (5 to 1 mole ratio), a 26% yield of nitroethanol was obtained. On chilling and seeding the residue from this reaction, a 42% yield of crude NPD could be isolated.

4. NPD diacetate was prepared in 80% yield from the crude NPD obtained from residues as in (3).

5. NPD diacetate could not be prepared directly from sodium NPD except in very low yields.

6. Methyl 4-nitrobutyrate could not be prepared by a column technique similar to that used in the preparation of nitroethanol.

7. Methyl 4-nitrobutyrate was prepared in 58% yield by the condensation of nitromethane and methyl acrylate in the presence of benzyltrimethylammonium hydroxide at reflux temperatures.

8. Cyclohexene gave a reaction with 20% nitric acid, 1000 pounds per square inch pressure, between 70°C and 130°C. With 67% nitric acid under these conditions, destructive oxidation took place.

II. TECHNICAL PROGRESS

A. INTRODUCTION

The present program is directed towards the industrial development of nitropolymer starting materials and intermediates. Nitroethanol,

nitropropanediol, and methyl 4-nitrobutyrate have been studied with process development as the main object. The investigation of the liquid phase nitration of cyclohexene has been started.

B. PREPARATION OF NITROETHANOL

1. Discussion

The preparation of nitroethanol by a batch method gives yields of 31-50%.[1]

Equation 1

$$CH_3NO_2 + CH_2O \longrightarrow \underset{\text{I}}{NO_2-CH_2-CH_2OH} + \underset{\text{II}}{NO_2-CH-(CH_2OH)_2} + \underset{\text{III}}{NO_2-C-(CH_2OH)_3}$$

As the by-products II and III need additional formaldehyde, one means of decreasing their production is a large excess of nitromethane. This has been achieved by using a column as the reactor with the nitromethane being continually refluxed.[2] As nitroethanol is formed it descends the column and the catalyst is neutralized. Using a 2 in. by 4 ft. column packed with stainless steel saddles, average yields of 66% of nitroethanol were obtained.

The reaction was studied at 200 mm. of mercury pressure, where yields were 20-30% as compared to 66% at atmospheric pressure. A column shorter than 4 ft. gave a lower yield. More compact packing lowered the amount of nitromethane refluxed, thus lowering the yield.

2. Experimental

A 2 in. by 4 ft. heated column, packed with stainless steel saddles, was fitted at the top with a reflux condenser through which a dropping funnel introduced the basic formaldehyde solution. Ten moles (610 g.) of nitromethane with 150 ml. of water and 20 ml. of 1 normal hydrochloric acid were placed in the still pot and refluxed strongly. The 4 moles (300 ml.) of 37% formaldehyde solution, made basic with 5.5 ml. of 10% sodium carbonate, were added so that the mole ratio of nitromethane to formaldehyde was 75-85 to 1 in the reaction zone.

---

1. Aerojet Report No. 461, July 20, 1950.

2. U. S. P. 2,510,914.

After the addition was complete the reaction mixture was evaporated at 50 mm. until the liquid temperature rose to 65°C. The residue was azeotropically distilled with phenyl ether at reduced pressure. After extracting the nitroethanol layer with n-hexene to remove dissolved phenyl ether, there was obtained 240 g. (2.64 moles, 66%) of 2-nitroethanol. Five moles of nitromethane were recovered.

C. PREPARATION OF 2-NITROPROPANEDIOL-1,3 (NPD)

1. Discussion

By equation 1, NPD (II) can be prepared. Gorsky states that the maximum yield of NPD is when the starting mole ratios of nitromethane to formaldehyde are 5-1.[3] This value is in agreement with our data. Purification is the most difficult problem in this method. Nitroethanol can be stripped off by the use of a falling film evaporator, the residue from which yields a technical grade of NPD. The crude material can be recrystallized from several solvents, butanol seems to be desired, but recoveries are not too good. This method of preparation is hazardous and the product still contains some tris(hydroxymethyl)nitromethane.

The NPD can be prepared free of nitroethanol and tris(hydroxymethyl)nitromethane by first forming the sodium salt of NPD, followed by acidification and extraction.

Equation 2

Step 1

$$CH_3NO_2 + 2CH_2O + NaOH \longrightarrow C(CH_2OH)_2(NO_2Na)$$

IV

Step 2

$$C(CH_2OH)_2(NO_2Na) + \tfrac{1}{2}H_2SO_4 \xrightarrow{\text{Urea}} H\text{-}C(CH_2OH)_2(NO_2) + \tfrac{1}{2}Na_2SO_4$$

II

---

3. Gorsky, I. M., and Makarov, S. P., Ber., 67B, 996 (1934).

Various acids have been used in step 2 but the presence of urea or hydroxylamine seems to be beneficial.[4] Dilute sulfuric acid (15%) in the presence of urea proves to be the most economical reagent.

The NPD can be continuously extracted from the aqueous solution with ethyl ether to give a product of good quality, but 24 hr. are required for this operation. The NPD can be extracted with ethyl acetate in a four-step batch extraction rapidly, the product from which is acceptable but not as good in color or melting point as from the ether extraction.

Attempts were made to free the NPD from the sodium salt or the calcium salt in nonaqueous media. No satisfactory method was found.

The sodium NPD was acidified by passing a water solution through an acid resin column. The ether extract of the resulting solution gave a poor quality material in 20% yield.

2. Experimental

To a stirred mixture of 122 g. (2.0 moles) of nitromethane, 300 ml. (4.0 moles) of 37% formaldehyde solution, 100 ml. of water, and 250 ml. of methanol in a flask surrounded by an ice bath was added dropwise 90 g. (2.0 moles) of sodium hydroxide in solution in 180 ml. of water. The salt precipitated. The slurry was stirred for 2 hr. and filtered at 0°C. The filter cake was returned to the reaction flask and ice bath, made a slurry with 100 ml. of water and 25 g. of urea added. The pH was slowly brought to 3.5-4.0 with 15% sulfuric acid. The solution was filtered to remove precipitated sodium sulfate and was then extracted four times with ethyl acetate. To remove dissolved water, 100 ml. of ethanol was added to form the low boiling ethyl acetate-ethanol-water azeotrope and the solution was evaporated. The remaining oil was chilled and seeded to obtain 81.0 g. (0.67 mole, 33.5%) of light colored, solid NPD, m.p. 50-52°C. A second crop was obtained, 31.5 g. (0.26 mole, 13%), that was darker in color, m.p. 42-46°C. The total yield of two crops was 46.5%.

D. PREPARATION OF METHYL 4-NITROBUTYRATE

1. Discussion

This study was concerned with the following reaction:

Equation 3

$$CH_3NO_2 + CH_2 = CH\text{-}COOCH_3 \xrightarrow{\text{base}} \underset{\text{V}}{NO_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOCH_3} + \underset{\text{VI}}{NO_2\text{-}CH\text{-}(CH_2\text{-}CH_2\text{-}COOCH_3)_2} + \underset{\text{VII}}{NO_2\text{-}C\text{-}(CH_2\text{-}CH_2\text{-}COOCH_3)_3}$$

4. Kornblum, N., and Graham, G. E., J. Am. Chem. Soc., 73, 4041 (1951).

The yields of by-products VI and VII can be decreased by using a large excess of nitromethane. To do this, a column type reactor was tried, but no conditions were found which gave satisfactory yields. Kloetzel[5] found triethylamine one of the best catalysts for this type of reaction. With triethylamine at room temperature, we obtained 15% yield of product after 2 days, 34% after 4 days, and 42% after 9 days. When methyl isopropylamine was used as the catalyst and the reaction refluxed for 1 hr., 43.5% of product was obtained. When benzyltrimethylammonium hydroxide was the catalyst and the reaction was refluxed for 2 hr., the yield was increased to 58%.

2. Experimental

One mole (86 g.) of stabilized methyl acrylate, 610 g. (10 mole) of washed nitromethane, and 10 ml. of 40% benzyltrimethylammonium hydroxide in water solution were refluxed together for 2 hr. The reaction mixture was washed with 100 ml. of water containing 5 ml. of 6 normal hydrochloric acid. After evaporating the nitromethane solution at reduced pressure, the residue was distilled to obtain 86.0 g. (0.585 mole, 58.5%) of methyl 4-nitrobutyrate at 85°-100°C (1-2 mm.).

E. LIQUID PHASE NITRATION OF CYCLOHEXENE

In an attempt to obtain some nitro or polynitro compounds, the liquid phase nitration of cyclohexene was undertaken. In preliminary runs, 67% nitric acid at 1000 p.s.i. pressure gave predominately oxidation at any temperature above room conditions. With 20% nitric acid at 1000 p.s.i. pressure, reaction started when the temperature was raised to 60°C and became violent above 140°C. Runs were then made at 70°, 100°, and 120°C. The solid which was obtained from the 70°C run, and the oils from the higher runs, are being identified.

5. Kloetzel, M. C., CSC Report, C.R.M.R.-1534 (1945).